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Is Vanadate Reduced by Thiols under Biological  
Conditions?: Changing The Redox Potential of  
V(V)/V(IV) by Complexation in Aqueous solution

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**Estimation of V(V)/V(IV) redox potential at pH 7.** Direct V(V)/V(IV) redox potential measurement is only possible in acidic solutions,<sup>1</sup> where V(V) and V(IV) exists as  $\text{VO}_2^+$  and  $\text{VO}^{2+}$ , respectively, so any other values have been calculated. In the following section we describe such estimation based on updated and accepted V(V) and V(IV) species formation constants and solubility products. Redox potential ( $E$ ) dependence on solution pH, such as Pourbaix diagram (Figure 1 in Ref. 2) is generally used for redox estimation at neutral pH. Reaction (1) redox potential as a function of pH<sup>3</sup> and species concentration is shown in the equation (2).



$$E = 1.004 - 0.1182 \cdot \text{pH} + 0.0591 \cdot \log([\text{VO}_2^+]/[\text{VO}^{2+}]) \quad (2)$$

At neutral pH redox potential will be attenuated in two ways: by the pH, and by both V(V) and V(IV) aqueous hydrolysis equilibria, since neither  $\text{VO}_2^+$  nor  $\text{VO}^{2+}$  exist in solution at pH 7. Aqueous V(V) and V(IV) speciation is well-characterized by potentiometry and confirmed by spectroscopic (<sup>51</sup>V NMR, EPR, and UV) methods. The V(V) predominant monomeric species at pH 7.0 is monoanion  $\text{H}_2\text{VO}_4^-$ , and the well established equilibrium (3) constant is equal<sup>4</sup> to  $10^{6.74} \text{ M}^{-2}$ .



The V(IV) predominant species at pH 7.0 depends upon the total concentration of V(IV) (Figure 6 in Ref. 2). In an aqueous solution without chelating ligands the  $\text{VO}(\text{OH})_2$  solubility is limiting the amount of soluble (VI) species, which include  $(\text{VO})_2(\text{OH})_5^-$  and  $\text{VO}(\text{OH})_3^-$ . The  $\text{VO}(\text{OH})_2$  solubility product value (eq. 4) is equal<sup>5</sup> to  $6.6 \cdot 10^{-23} \text{ M}^3$ .



After the predominant V(V) and V(IV) species are substituted into equation 1, the redox equilibrium at neutral pH becomes as shown in equation 5, with pH dependence given in equation 6.



$$E = 1.000 - 0.1182 \cdot \text{pH} + 0.0591 \cdot \log[\text{H}_2\text{VO}_4^-] \quad (6)$$

For specific conditions, when total vanadium(V) concentration is equal to 1 mM, the  $[\text{H}_2\text{VO}_4^-]$  is equal to 0.43 mM at pH 7, and  $E = -0.026 \text{ V}$ .

## References

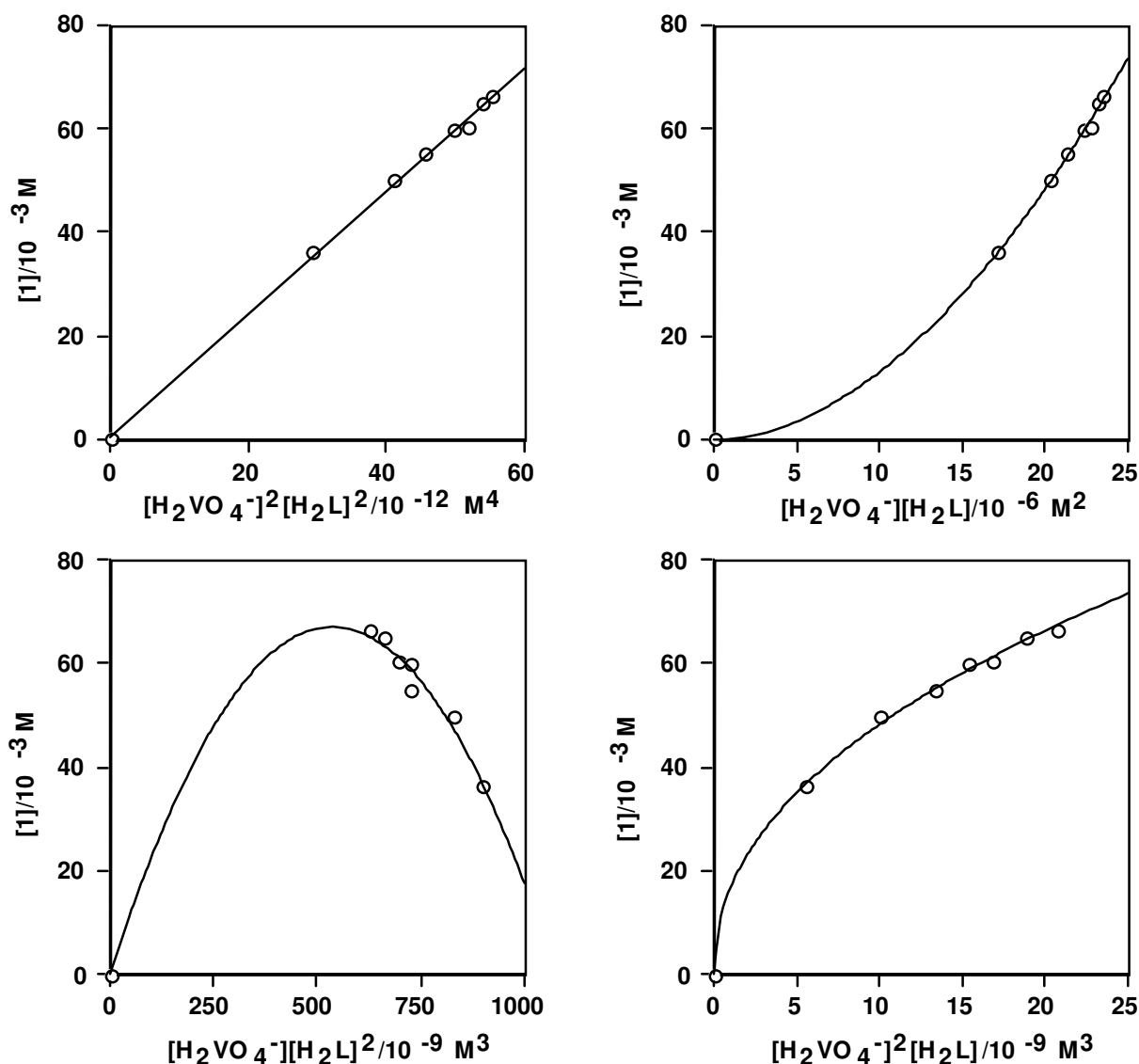
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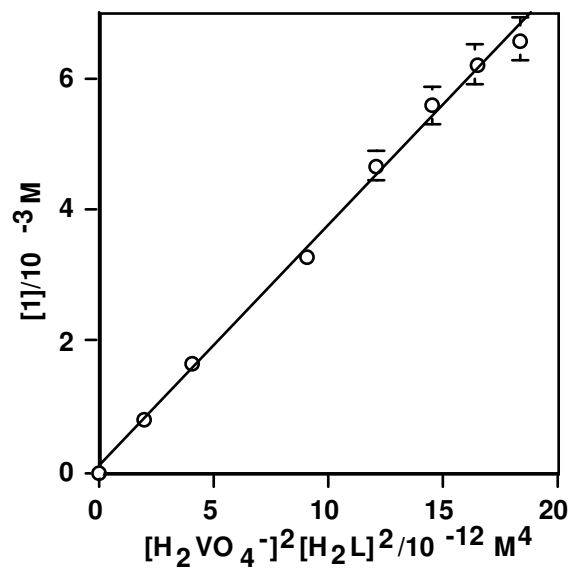
**Table 1S.** Molar percent of vanadium species in solution containing 2-mercaptoethanol (10 mM) and both 1.0 mM or 1  $\mu$ M vanadium(V) and vanadium(IV).

Species <sup>a</sup>	1 mM <sup>b</sup> V(V) and V(IV)			1 $\mu$ M <sup>b</sup> V(V) and V(IV)		
	pH = 6	pH = 7	pH = 8	pH = 6	pH = 7	pH = 8
$[(VO_2)_2L_2^{2-}]$	76.0	74.6	63.6	2.22	1.96	0.76
$[(VO_2)_4L_4^{4-}]$	0.16	0.15	0.11	$1.4 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$	$1.6 \cdot 10^{-8}$
$[V_1]$	19.2	20.4	31.2	97.7	98.0	99.2
$[V_2]$	3.42	3.36	4.09	0.088	0.078	0.030
$[V_4]$	1.22	1.18	0.94	$8.1 \cdot 10^{-7}$	$6.3 \cdot 10^{-7}$	$9.6 \cdot 10^{-8}$
$[VOL_2^{2-}]$	$7.6 \cdot 10^{-7c}$	$7.6 \cdot 10^{-5c}$	$4.4 \cdot 10^{-3}$	$7.9 \cdot 10^{-5}$	$4.2 \cdot 10^{-3}$	0.13
$[(VO)_2(OH)_5^-]$	$2.76^c$	$27.6^c$	98.8	29.7	85.0	67.2
$[VO(OH)_3^-]$	$0.021^c$	$0.21^c$	1.25	2.17	11.6	32.6
$[VOOH^+]$	$0.59^c$	$0.059^c$	0.035	61.1	3.27	0.092
$[VO^{2+}]$	$0.066^c$	$6.6 \cdot 10^{-4c}$	$4.0 \cdot 10^{-6}$	6.9	0.037	$1.0 \cdot 10^{-4}$
Ratio <sup>d</sup>	$1.0 \cdot 10^8$	$9.9 \cdot 10^5$	$1.5 \cdot 10^4$	$2.8 \cdot 10^4$	$4.7 \cdot 10^2$	6.1

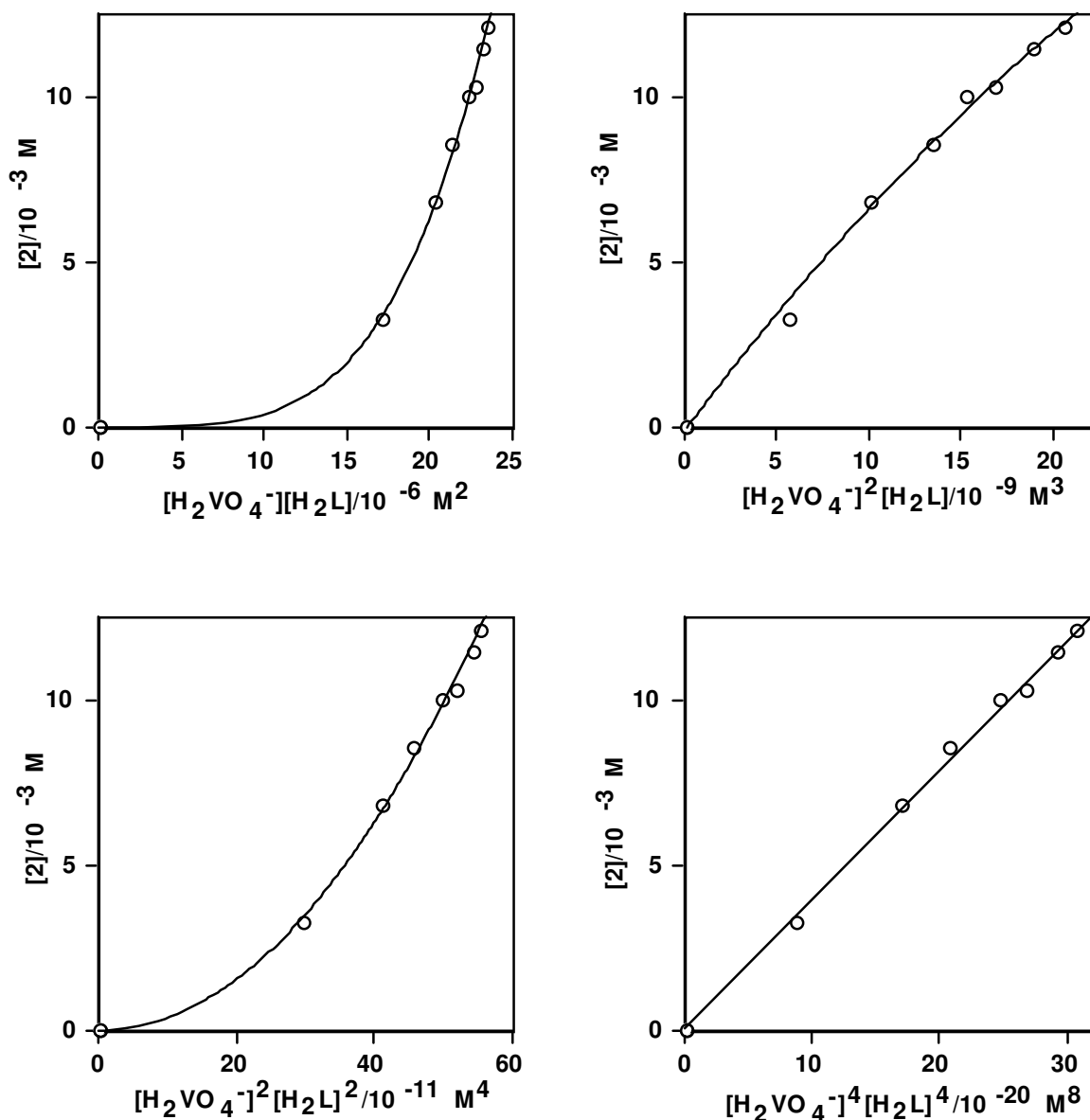
<sup>a</sup>L<sup>2-</sup> denotes the (OCH<sub>2</sub>CH<sub>2</sub>S)<sup>2-</sup> group; <sup>b</sup>total concentration of vanadium(V) or total concentration of vanadium(IV); <sup>c</sup> insoluble [VO(OH)<sub>2</sub>] present in solution ( $K_{sp} = 6.6 \cdot 10^{-23} \text{ M}^3$ )<sup>53</sup>  
<sup>d</sup>ratio of  $(2 [(VO_2)_2L_2^{2-}] + 4 [(VO_2)_4L_4^{4-}]) / [(VO)L_2^{2-}]$ .



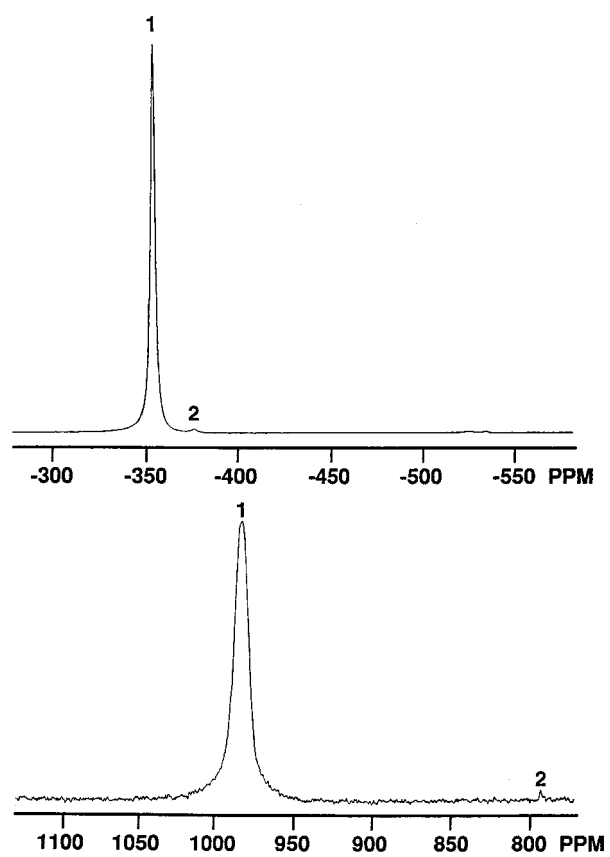
**Figure S1.** Plot of complex **[1]** (-362 ppm) as a function of  $[H_2VO_4^-]^2[H_2L]^2$  (here  $H_2L = HOCH_2CH_2SH$ ) at high ionic strength. The linear relationship between **[1]** and  $[H_2VO_4^-]^2[H_2L]^2$  indicates a 2:2 complex stoichiometry for **1**. Data points obtained by quantitative  $^1H$  and  $^{51}V$  NMR spectroscopy in solutions containing vanadate (0.1 to 0.275 M) and 2-mercaptoethanol (0.15 M) in the presence of 3 M KCl.



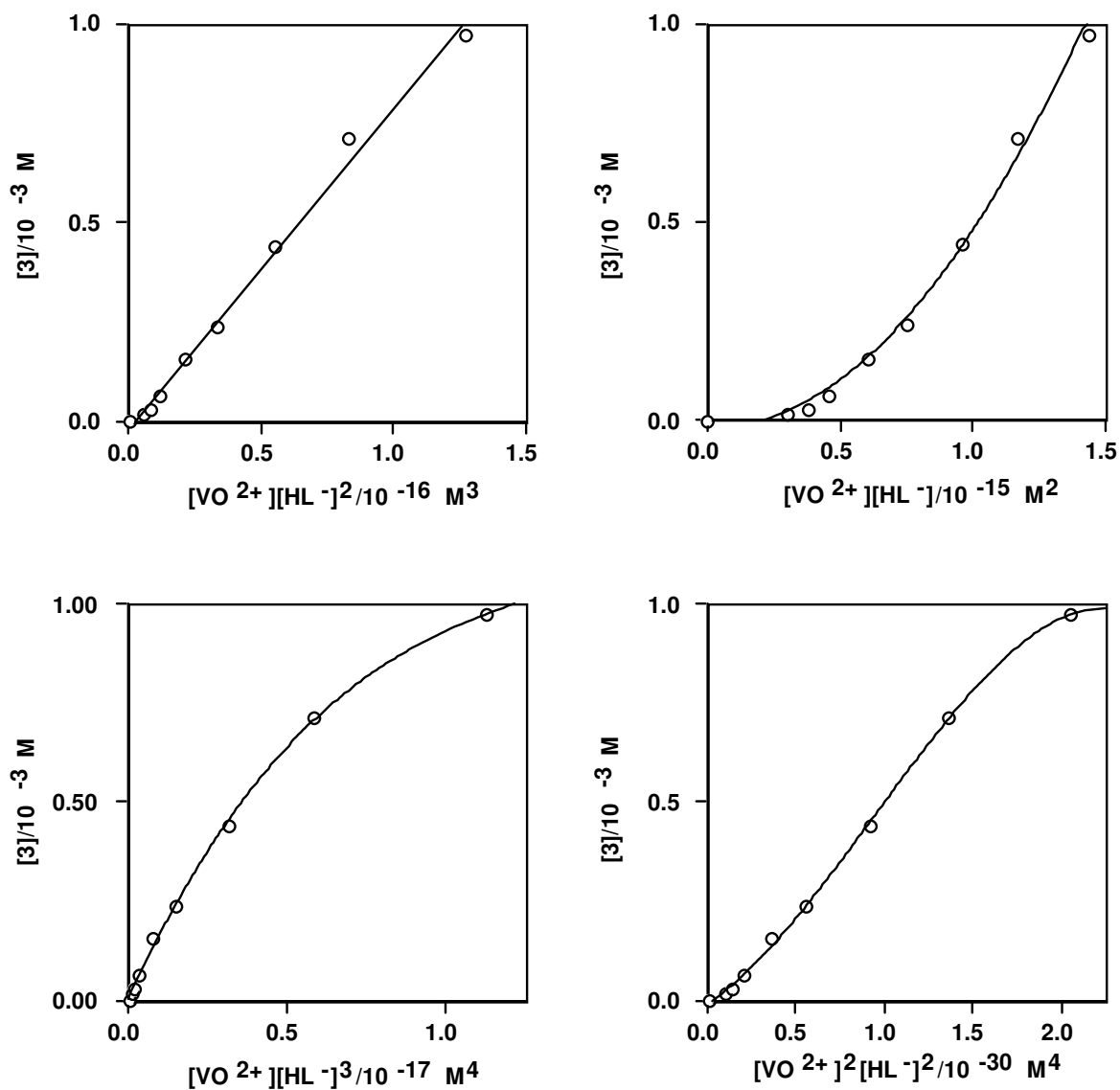
**Figure S2.** Plot of the complex **[1]** (-362 ppm) as a function of  $[H_2VO_4^-]^2[H_2L]^2$  (here  $H_2L = HOCH_2CH_2SH$ ). The linear relationship between **[1]** and  $[H_2VO_4^-]^2[H_2L]^2$  indicates a 2:2 complex stoichiometry for **1**.



**Figure S3.** Plots of the complex **[2]** (-385 ppm) as a function of  $[H_2VO_4^-][H_2L]$ ,  $[H_2VO_4^-]^2[H_2L]$ ,  $[H_2VO_4^-]^2[H_2L]^2$ , and  $[H_2VO_4^-]^4[H_2L]^4$  (here  $H_2L = HOCH_2CH_2SH$ ). The linear relationship between **[2]** and  $[H_2VO_4^-]^4[H_2L]^4$  indicates a 4:4 complex stoichiometry for **2**.

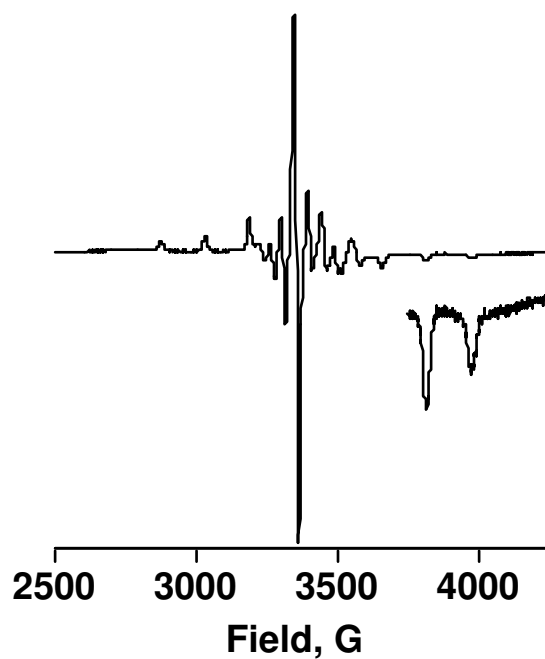


**Figure S4.** The  $^{51}\text{V}$  (top) and  $^{17}\text{O}$  (bottom) NMR spectrum recorded in a solution containing vanadate (300 mM) and 2-mercaptoethanol (600 mM) at pH 8.6.



**Figure S5.** Plots of complex **[3]** in borate buffer at pH 9.6 as a function of  $[\text{VO}(\text{H}_2\text{O})_5^{2+}][\text{HL}^-]$ ,  $[\text{VO}(\text{H}_2\text{O})_5^{2+}][\text{HL}^-]^2$ ,  $[\text{VO}(\text{H}_2\text{O})_5^{2+}][\text{HL}^-]^3$  and  $[\text{VO}(\text{H}_2\text{O})_5^{2+}]^2[\text{HL}^-]^2$  (here  $\text{HL}^- = \text{HOCH}_2\text{CH}_2\text{S}^-$ ). The linear relationship between **[3]** and  $[\text{VO}(\text{H}_2\text{O})_5^{2+}][\text{HL}^-]^2$  indicates a 1:2 complex stoichiometry for **3**.





**Figure S6.** Representative EPR spectrum is shown for frozen (170 K) “solution” of  $\text{VOSO}_4$  (10 mM) and 2-mercaptoethanol (0.2 M) at pH 9.6. High-field range (3750 – 4250 G) shown on the inset indicates that only one EPR active species ( $[\text{VO}(\text{OCH}_2\text{CH}_2\text{S})_2]^{2-}$ ) is present at detectable level.